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(56) Documents cited

Maiti et al Solid State Ionics 13, pp 285-292 (1984).

J. Power Sources 14 pp 295-303 (1985)

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Selected US specifications from IPC sub-class

C01F

(54) **Barium cerate doped with gadolinium**

(57) A doped barium cerate-based solid electrolyte for use in electrochemical devices wherein the dopant is gadolinium. The perovskite material is useful in electrochemical devices.

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PEROVSKITE COMPOUNDS

The present invention relates to rare earth doped barium cerates of the perovskite structure and the use thereof as ionic conductors in electrochemical devices in general and in fuel cells in particular.

5 Fuel cells are electrochemical devices in which the chemical energy of a conventional fuel is converted into low voltage, direct current electrical energy.

Fuel cells using liquid electrolytes normally operate at low temperatures and require relatively expensive fuels containing low
10 levels of carbon monoxide, such as hydrogen, to generate electrical energy. Hence, attention has been turned to the use of solid, ceramic electrolytes which can be operated at higher temperatures thus exhibiting higher tolerance for carbon monoxide and enabling the use of relatively cheaper fuels such as fossil fuels. In order
15 to be technically or commercially viable such solid electrolytes should essentially have:

- (a) good oxide ion conductivity and negligible electronic conductivity at the operating conditions,
- (b) adequate mechanical strength, and
- 20 (c) an easy fabrication process.

Several complex metal oxides when used as solid electrolytes possess one or more of the above desirable characteristics. Typical amongst these are the oxides having a fluorite structure, e.g. $\text{ZrO}_2\text{:Y}$ or $\text{CeO}_2\text{:Gd}$, or perovskite structure, e.g. $\text{CaTiO}_3\text{:Mg}$ or
25 $\text{BaCeO}_3\text{:Y}$.

Takahashi et al in Energy Conversion, 11, pp 105-11 (1971), have measured the ionic conductivities of a number of doped perovskites. For example $\text{CaTiO}_3\text{:Mg}$ exhibited a specific ionic conductivity of approximately $4 \times 10^{-3} \text{ ohm}^{-1}\text{cm}^{-1}$ at 800°C . A fuel cell incorporating the above electrolyte and operating at 1000°C delivered a current density of 25 mA cm^{-2} at 0.7V .

Iwahara et al in Solid State Ionics, 3/4, pp 359-63, (1981) and in J. Power Sources, 7, pp 293-301 (1982) report the results of their studies on the use of strontium cerate, SrCeO_3 , doped with yttrium, yttrium or magnesium as solid electrolytes in fuel cells. They concluded that such systems were protonic conductors on the basis of EMF measurements in oxygen and hydrogen concentration cells as well as in fuel cells. A fuel cell incorporating a $\text{SrCeO}_3\text{:Yb}$ pellet approximately 0.5 mm thick achieved current densities of 20 mA cm^{-2} and 50 mA cm^{-2} at 800° and 1000°C respectively at a terminal voltage of 0.7V .

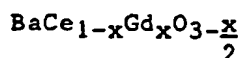
Further investigations on solid electrolytes of the ceria based perovskites type are reported by Maiti et al in Solid State Ionics, 13, pp 285-292 (1984) and J. Power Sources, 14, pp 295-303 (1985). These authors used systems containing barium cerate, BaCeO_3 , doped with each of yttrium, lanthanum, holmium and neodymium and found that these systems had high oxide ion conductivity; notably $\text{BaCeO}_3\text{:Y}$ had an oxide ion conductivity of $5 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 800°C . From a systematic study of the oxygen partial pressure dependence of the conductivity, these authors determined the ionic transport numbers for such systems to be about 0.5 in air at 800°C .

Thus, the reported specific ionic conductivities of perovskites indicate that these materials will only be suitable for use in solid state fuel cells operating at over 800°C . Consequently, the materials cost for constructing fuel cells based on the above electrolytes would render them commercially unattractive.

It is therefore the object of the present invention to develop solid electrolytes of the perovskite type which are capable of operation at temperatures significantly below 800°C without substantial loss of conductivity and performance of the fuel cell.

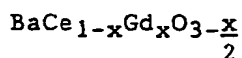
Accordingly, the present invention is a doped barium cerate-based solid electrolyte for use in electrochemical devices characterised in that the dopant is gadolinium.

According to another embodiment the present invention is a solid electrolyte for use in an electrochemical device, said electrolyte having the composition:



where x represents the amount of the dopant gadolinium ions replacing the cerium ions in the BaCeO_3 lattice.

According to a further embodiment the present invention comprises an electrochemical device which has a solid electrolyte of the perovskite structure having an oxide ion conductivity from 0.13×10^{-3} at 200°C to 38×10^{-3} at 800°C characterised in that the solid electrolyte is a gadolinium doped barium cerate of the formula:



wherein x is the amount of the dopant gadolinium ions replacing the cerium ions in the BaCeO_3 lattice.

The value of x quoted herein is in terms of atom fraction, based on the combined number of gadolinium and cerium atoms in the mixed oxide composition.

The solid gadolinium doped barium cerates will hereafter be referred to as "BCG" for convenience.

The amount of dopant gadolinium ion 'x' in the solid electrolyte is suitably from 0.01 to 0.30 atom fraction, preferably from 0.10 to 0.20 atom fraction.

The solid electrolytes of the present invention can be used in electrochemical devices such as fuel cells, oxygen gas monitor and electrosynthetic cells. The solid electrolytes can be used in a variety of shapes. In the present context, the performance of the electrolyte was tested in the shape of pellets in a fuel cell but is not intended to be limited either to such shapes or for use in fuel cells. With this proviso, the solid electrolyte doped with

gadolinium may be prepared for instance as follows in a sequence of steps which include oxide preparation, ball milling, pressing and sintering.

(a) Oxide Preparation

5 In view of the difficulties in handling barium oxide which readily absorbs carbon dioxide and water from the atmosphere, the mixed oxides were prepared by heating a mixture of a barium compound, which readily decomposes into the oxide in situ, with the other oxides, enabling a reaction between the oxides.

10 The appropriate amounts of the starting materials (BaCO_3 , CeO_2 and Gd_2O_3) are suitably ground together and heated e.g. in air at elevated temperature e.g. 1100°C .

The composite powders so formed are preferably re-ground and heated e.g. at about 1400°C in air for a further extended period to
15 achieve completion of reaction. It is preferable to check the mixed powder at this stage e.g. by X-ray powder diffraction analysis to ensure that the products show a pure BaCeO_3 -type phase.

(b) Ball-milling

The powder product from step (a) is suitably ground again in a
20 ball mill for a short period and sieved using an appropriate sieve. The particle size distribution of the desired powder is suitably in the range of 5-40 micrometers.

(c) Pressing

The sieved powders from step (b) can be made into a uniform
25 paste using a liquid medium well known for this purpose in the art, e.g. ethylene glycol, glycerine and the like, and pelletised e.g. by pressing in a pellet die. It is suitably pressed for about 1 minute at a pressure of 4 tons/cm^2 so as to achieve a compactness (or relative density) of at least 90% and an inter-connected porosity
30 value not greater than 1%. Pellets so formed are dried e.g. for 2 hours under an infra-red lamp.

(d) Sintering

The pellets from step (c) are sintered e.g. for about 10 hours at elevated temperature e.g. 1475°C . The sintering may be carried
35 out in an oxidising or a reducing atmosphere, suitably in a reducing

atmosphere, preferably using 5% hydrogen in nitrogen. Subsequently the sintered product is cooled gradually.

In the case where the final sintering step is carried out in an oxidising atmosphere, e.g. air, the final product has a darkish appearance. However, the product sintered in a reducing atmosphere is virtually white in colour.

The ionic conductivity and the ionic transport number of the solid electrolytes of the present invention may be measured by impedance spectroscopy carried out over a range of oxygen partial pressures.

The technique for impedance spectroscopy for the measurement of the ionic conductivity offers the advantage of enabling the bulk conductivity to be resolved from resistive and capacitive effects arising at grain boundaries within the material and at the electrode/material interface.

By contrast, two terminal measurements, performed using d.c. or fixed frequency a.c. will give misleading results regarding the bulk properties, as a result of these resistive and capacitive effects.

In practice, impedance spectroscopy involves measurement of the real and imaginary parts of the impedance over a range of frequencies, e.g. using an a.c. bridge, and plotting the results, e.g. as imaginary versus real impedance.

Although existing ceria-based electrolytes (e.g. ceria-gadolinia) possess the required ionic conductivity for fuel cell applications, it is known that in the reducing environment encountered at the anode of a fuel cell, such electrolytes acquire partial electronic conductivity with consequent loss of fuel cell voltage. (cf. P.N. Ross and T.G. Benjamin, J. Electrochem Soc, 122, 255-9 (1975)). However, we have found that BCG-based electrolytes are highly resistant to reduction by hydrogen at 800°C and are thus very stable thereby underlining their suitability for use in hydrogen-oxygen fuel cells. The BCG pellets of the present invention are particularly suited for fuel cells operating at 550-650°C.

The present invention is further illustrated with reference to

the following Examples.

Examples

1. Preparation and Characterisation of BCG Pellets

5 In the preparation of samples the following sequence of operations was followed to ensure that pellets were of the correct composition and phase purity, and of sufficiently low gas permeability.

(a) Oxide Preparation

10 Starting materials (BaCO_3 , CeO_2 and Gd_2O_3) used in varying amounts as shown in Table 1 below were ground together in an agate mortar for a minimum of 10 minutes and heated in an alumina crucible for 10 hours at 1100°C .

15 The resultant powders were re-ground and heated for a further 10 hours at 1400°C . X-ray powder diffraction analysis of products showed a pure BaCeO_3 -type phase.

(b) Ball-milling

20 Powders from step (a) were ground in an agate ball mill (FRITSCH, Model Pulverisette 7) for 30 minutes and sieved using a 42 micrometers sieve. Particle size analysis showed a size distribution in the range 5-40 micrometers.

(c) Pressing

25 Powders from step (b) were made into a uniform paste using ethylene glycol and pressed in a pellet die for 1 minute at a pressure of 4 tons/cm^2 . Pellets were dried for 2 hours under an infra-red lamp.

(e) Sintering

30 Pellets from step (d) were packed in coarse powders of their own composition, sintered for 10 hours at 1475°C in an atmosphere of 5% hydrogen in nitrogen. Subsequent cooling was restricted to a rate of 5°C/minute in order to avoid excessive thermal stress in the pellets.

Table 1
Weight in grams of Starting Materials used to Prepare the Family
of Compounds $\text{BaCe}_{1-x}\text{Gd}_x\text{O}_{3-x}$

	<u>BaCO₃</u>	<u>CeO₂</u>	<u>Gd₂O₃</u>	<u>x</u>
5	10.00	8.289	0.4592	0.05
	10.00	7.854	0.9184	0.10
	10.00	7.417	1.3776	0.15
	10.00	6.980	1.8367	0.20
10	10.00	6.544	2.2959	0.25
	10.00	6.108	2.7552	0.30

2. Results

2.1 X-ray Powder Diffraction results

The products of the above preparation were subjected to X-ray powder diffraction analysis using a copper K-alpha radiation, which showed them to be predominantly of a perovskite structure. The d-spacings and relative peak heights are given in Table 2 for $x = 0.10$. The same d-spacings are found in samples of BCG for values of x in the range 0 to 0.30 (inclusive), in varying degrees of sharpness.

Table 2

Main lines in the X-ray diffraction pattern of BCG for $x = 0.10$. The above lines are found in samples of BCG for values of x in the range 0 to 0.30 in varying degrees of sharpness.

	<u>d-Spacing (Å)</u>	<u>Peak Height</u>
	4.40	< 1
	3.11	100
	2.654	< 1
5	2.541	< 1
	2.203	14
	2.194	9
	1.800	10
	1.795	19
10	1.56	1
	1.555	10
	1.393	4
	1.389	5

2.2 Conductivity Results

15 Metallic electrodes of silver or platinum pastes (Johnson
Matthey P-2100 and E-8210) were applied to the pellet faces and
baked at temperatures of 400°C and 1000°C respectively. Impedance
spectra were obtained over the frequency range 5 Hz to 13 MHz using
an impedance analyser (HP 4192A). The conductivity of BCG was
20 studied as a function of temperature in air and isothermally as a
function of oxygen partial pressure (P_{O_2}). Partial pressures were
fixed using column-dried nitrogen/oxygen and nitrogen/hydrogen gas
mixtures of pre-determined ratios. An equilibration period of 1-2
hours was allowed between each set of measurements, after which
25 stable conductivities were obtained. For hydrogen/nitrogen
mixtures, the P_{O_2} was determined using a zirconia oxygen monitor
made from a $ZrO_2:Y$ tube with platinum electrodes and operated at
600°C using pure oxygen as a reference atmosphere.

Impedance spectra were obtained on samples of BCG for $x = 0.05$
30 to $x = 0.30$ over the temperature range 200 to 800°C.

The spectra for $x = 0.1$ at 200 and 600°C, given in Tables 3 and
4, illustrate the behaviour of BCG at low and high temperatures
respectively.

When plotted in the complex plane, the impedance data in
35 Table 3 resolve a semi-circle passing through the origin,

characteristic of the bulk resistivity, and an oblique line due to the electrodes.

Similarly, the data in Table 4 resolve part of a semi-circle, characteristic of the bulk resistivity, and the electrode impedance.

5

Table 3

Experimental Impedance Spectrum, Corrected for Sample Shape,
obtained for a pellet of BCG (x=0.1) with Silver Paste
Electrodes at 200°C

	<u>Frequency</u> (Hz)	<u>Impedance, Real Part</u> (ohm cm)	<u>Impedance, Imag. Part</u> (ohm cm)
10	100.0	54624	47209
	158.5	43203	38787
	251.2	34355	31757
	398.1	27525	25486
15	631.0	22379	20101
	1000.0	18556	15685
	1584.9	15683	12198
	2511.9	13455	9500
	3981.1	11683	7411
20	6309.6	10268	5765
	10000.0	9159	4453
	15848.9	8307	3404
	25118.9	7669	2564
	39810.7	7218	1898
25	63095.7	6914	1388
	100000.0	6724	1027
	158489.3	6606	796
	251188.6	6532	684
	398107.1	6468	687
30	630957.3	6398	811
	1000000.0	6279	1077
	1584893.0	6035	1507
	2511886.0	5549	2067
	3981071.0	4708	2615
35	6309573.0	3543	2884
	10000000.0	2323	2707

Table 4
Experimental Impedance Spectrum, Corrected for Sample Shape,
obtained for a pellet of BCG (x=0.1) with Silver Paste
Electrodes at 600°C

5	<u>Frequency</u>	<u>Impedance, Real Part</u>	<u>Impedance, Imag. Part</u>
	(Hz)	(ohm cm)	(ohm cm)
	5.0	142.8	13.2
	6.3	141.1	12.6
	10.0	137.9	11.6
10	15.8	134.8	10.9
	25.1	131.8	10.3
	39.8	129.0	9.8
	63.1	126.2	9.5
	100.0	123.5	9.2
15	158.5	120.9	9.1
	251.2	118.3	8.9
	398.1	115.8	8.7
	631.0	113.3	8.7
	1000.0	110.7	8.6
20	1584.9	108.2	8.5
	2511.9	105.7	8.4
	3981.1	103.2	8.2
	6309.6	100.8	8.0
	10000.0	98.5	7.7
25	15848.9	96.3	7.4
	25118.9	94.3	7.2
	39810.7	92.4	7.2
	63095.7	90.5	7.4
	100000.0	88.6	7.8
30	158489.3	86.4	8.4
	251188.6	83.9	9.1
	398107.1	81.0	9.9
	630957.3	77.7	10.4
	1000000.0	74.4	10.6
35	1584893.0	71.2	10.4

Table 4 - Continued

Experimental Impedance Spectrum, Corrected for Sample Shape,
obtained for a pellet of BCG (x=0.1) with Silver Paste
Electrodes at 600°C

Frequency (Hz)	Impedance, Real Part (ohm cm)	Impedance, Imag. Part (ohm cm)
2511886.0	68.7	10.2
3981071.0	67.0	10.8
6309573.0	66.1	14.0
10000000.0	63.2	25.2

The bulk conductivity of BCG is given in Table 5 as a function of temperature and doping level x. It can be seen that at any one temperature the highest conductivity lies between those for the values of x = 0.1 and x = 0.2.

15

Table 5

Conductivity of BCG as a Function of Temperature and Doping Level x

x	Conductivity ($\times 10^{-3}$ ohm $^{-1}$ cm $^{-1}$)					
	200°C	400°C	500°C	600°C	700°C	800°C
0.05	0.091	-	3.9	8.0	15.4	30.3
0.10	0.134	3.6	7.8	14.7	24.4	38.5
0.20	0.122	3.9	9.0	13.1	-	37.3
0.30	0.0022	1.7	5.1	5.27	8.1	15.4

25

It can be seen from the data in Table 6 below that under comparable conditions the BCG system of the present invention exhibits a superior conductivity to that of the prior art (as described by Virkar and Maiti).

30

Table 6

Conductivity in air, of yttrium-doped barium cerate BaCe_{0.9}Y_{0.1}O_{2.9}
as determined by Virkar and Maiti in J. Power Sources 14, 295-303
(1985)* and in the present invention

Temperature (°C)	Conductivity ($\times 10^{-3}$ ohm $^{-1}$ cm $^{-1}$)		
	(Virkar & Maiti)* Reported Found		Present Invention
400	-	2.0	3.6
600	2.4	8.7	14.7
800	10	30	38.5

40

*Not according to the invention.

The conductivities extracted from the impedance data and tabulated above are total electrical conductivities and as such contain an ionic and an electronic contribution, the relative magnitudes of which are described by the ionic transport number.

The ionic and electronic contributions to the conductivity have been resolved by measurement of the dependance of the total conductivity on the oxygen partial pressure (P_{O_2}). It is known that the ionic conductivity is invariant with P_{O_2} , while the electronic part has either a positive P_{O_2} dependance (p-type) or a negative P_{O_2} dependance (n-type). For example, from the data for BCG ($x = 0.1$) at 600°C , given in Table 7, the ionic contribution was determined as $11 \times 10^{-3} \text{ ohm}^{-1}\text{cm}^{-1}$ while the electronic contribution, in pure oxygen, was determined as p-type and of the value $5.6 \times 10^{-3} \text{ ohm}^{-1}\text{cm}^{-1}$.

Table 7
Conductivity of BCG (x=0.1) as a Function of Oxygen Partial Pressure
(P_{O_2}) at a Temperature of 600°C

	Po ₂ (atm)	Conductivity ($\times 10^{-3}$ ohm ⁻¹ cm ⁻¹)
20	1	16.7
	0.20	13.9
	0.05	12.8
	0.02	12.5
25	0.001	10.8
	1.6×10^{-24}	11.4
	3.6×10^{-25}	11.5
	5.8×10^{-26}	11.6
30	1.7×10^{-26}	10.9
	3.2×10^{-27}	10.7
	10^{-27}	10.9

From similar conductivity Po_2 data obtained at a range of
35 temperatures, the ionic transport number was determined and is
presented in Table 8.

Table 8
Experimental Transport Number t_i for BCG ($x=0.1$) derived from
Measurement of the P_{O_2} -Dependence of the Conductivity
at 400 to 800°C

Temperature °C	t_i
400	0.96
500	0.89
600	0.66
800	0.41

Surprisingly, the p-type conductivity observed at high P_{O_2} does not affect the performance of BCG systems of the present invention when used as fuel cell electrolytes as will be shown below.

2.3 Construction and Operation of Fuel Cells

Hydrogen-oxygen fuel cells were constructed by applying metallic paste electrodes to both faces of a BCG pellet and sealing this to the end of a tube of re-crystallised alumina ceramic. Platinum (Johnson-Matthey P-2100) was used for the anode (H_2 electrode), while silver (Johnson-Matthe E-8210) was used for the cathode (O_2 electrode). Electrical connections were made to the electrodes by means of platinum leads. The assembly was mounted in a temperature controlled furnace and the temperature was monitored using a chromel-alumel thermocouple. The gases, dried oxygen and hydrogen were arranged to purge each compartment of the fuel cell. The current was set using a d.c. current source (Keithley model 220) while voltage measurements were carried out using a high impedance electrometer (Keithley model 617).

The voltage-current density performance using a BCG system ($x = 0.1$, thickness 0.42 mm) in a fuel cell at 600-800°C is reported in Table 9 below.

Table 9

Performance at 600, 700 and 800°C of a hydrogen-oxygen fuel cell based on a pellet of BCG ($x = 0.1$) of thickness 0.42 mm, with platinum anode and silver cathode

	600°C		700°C		800°C	
	I (mA cm ⁻²)	V (mV)	I (mA cm ⁻²)	V (mV)	I (mA cm ⁻²)	V (mV)
5	0	1105	0	1087	0	1028
	5	1037	25	938	25	958
10	10	964	50	752	50	885
	15	887	55	700	75	807
	20	803	75	503	100	764
15	25	712	100	210	125	634
	30	614	115	19	150	537
	35	508			175	430
	40	396			200	314
	45	282			225	188
20	50	165			250	50

It is a feature of the present invention that current densities of 25 mA cm⁻² at 600°C and 105 mA cm⁻² at 800°C are achieved at a terminal voltage of 0.7V. A cell of this type (where $x = 0.1$) when operated at 80 mA cm⁻² was stable for a test period of 1000 hours at 800°C.

For comparison with prior art solid electrolytes a ceria-gadolina (CG) system, hitherto believed to have the best ionic conductivity in a fuel cell, was compared as electrolyte with the BCG system of the present invention. The results of the CG system are tabulated in Table 10 below whereas those of the BCG system is shown in Table 11. It is clear from these results that the BCG system of the present invention is vastly superior to the prior art CG system in spite of

(a) using a relatively lower amount of gadolinium and

(b) using a greater thickness of the electrolyte,

which factors should normally adversely affect the results.

Table 10

Performance at 800°C of a hydrogen-oxygen fuel cell based on a
pellet of CG* (20% Gd) of thickness 0.9 mm with platinum
anode and silver cathode

5

10

15

Current Density (ma cm ⁻²)	Voltage (mV) CG
0	692
4	647
8	598
12	517
16	416
20	350
24	336

*Ceria-gadolina system (Not according to the invention).

Table 11

20

Performance at 800°C of a Hydrogen-oxygen fuel cell based on a
pellet of BCG (x = 0.1) of thickness 1.5 mm with platinum anode
and silver cathode

25

30

35

40

Current Density (ma cm ⁻²)	Voltage (mV) BCG
0	1089
5	1031
10	963
15	892
20	808
25	717
30	613
35	497
40	370
45	232
50	85

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Claims:

1. A doped barium cerate-based solid electrolyte for use in electrochemical devices characterised in that the dopant is gadolinium.

2. An electrolyte as claimed in claim 1, having the composition:

5 $\text{BaCe}_{1-x}\text{Gd}_x\text{O}_{3-x/2}$

where x represents the amount of the dopant gadolinium ions replacing the cerium ions in the BaCeO_3 lattice.

3. An electrochemical device which has a solid electrolyte of the perovskite structure having an oxide ion conductivity from
 10 0.13×10^{-3} at 200°C to 38×10^{-3} at 800°C characterised in that the solid electrolyte is a gadolinium doped barium cerate of the formula:

$\text{BaCe}_{1-x}\text{Gd}_x\text{O}_{3-x/2}$

where x represents the amount of dopant gadolinium ions replacing
 15 the cerium ions in the BaCeO_3 lattice.

20

25